Characterization of Deep Levels in Zn-Compound Semiconductors Grown by Molecular-Beam Epitaxy(分子線エピタキシ法で成長した亜鉛化合物半導体中の深い準位に関する研究)

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論文内容要旨

Zn-compound semiconductors such as ZnSe and ZnO are representative II-VI wide-bandgap semiconductors with direct bandgap, which makes the materials most promising for optical devices. The investigation of deep levels in Zn-compound semiconductors is an important issue, because highly-doped impurities degrade electrical and optical properties considerably through the formation of native and/or complex defects which give rise to deep levels in the bandgap. The deep levels trap minority/majority carriers and act as nonradiative centers that reduce carrier lifetime, thereby decreasing emission intensities in light-emitting devices. Furthermore, the deep levels may compensate carriers, which limit the attainable maximum carrier concentration below the level required for device fabrication. Such compensation becomes more serious as the bandgap increases and makes amphoteric doping very difficult. Therefore, the control of the deep levels is crucial when applying to optical devices. The purpose of this thesis is to characterize deep levels in Zn-compound semiconductors in particular in ZnSe and ZnO to contribute to the control of deep levels, which will eventually end up with the successful fabrication of optical devices.

ZnSe and ZnO layers were grown by molecular-beam epitaxy (MBE) which is considered to be most successful preparation methods. Characterization for the ZnSe and ZnO layers was performed using various methods including photoluminescence (PL), capacitance-voltage (C-V) measurements, deep-level-transient spectroscopy (DLTS), photocapacitance (PHCAP), current-voltage (I-V) measurements,

and admittance spectroscopy (AS).

First, we have investigated the deep levels and their characteristics of Al-doped ZnSe layers grown by MBE for the first time. Al is expected to be an ideal n-type source material for ZnSe due to its high purity and low chemical reactivity, compared to Cl which has the problems of corrosion and memory effect. Most of all, this work has been focused on the deep levels in heavily doped ZnSe layers that are degraded structurally, electrically, and optically, while previous researches were concentrated on undoped ZnSe and lightly-doped ZnSe. Heavy doping in ZnSe layers generates many types of deep levels due to the various origins and induced anomalous behaviors not found in undoped and lightly doped ZnSe, which makes it difficult to analyze deep levels. However, it is important to directly investigate the heavily doped materials where deep levels actually influence material and device properties.

(1) It was found that heavily doped ZnSe:Al layers exhibit two radiative trap centers RD1 and RD2 above the valence-band maximum (VBM). RD2, which shows strong deep-level emission at around 2.25 eV, was dominant in relatively lightly doped ZnSe:Al layers. RD2, which shows strong deep-level emission at around 1.97 eV, was dominant in relatively heavily doped ZnSe:Al layers. RD1 and RD2 are expected to be due to an Al_{Zn} complex defect and a V_{Zn}-related defect, respectively.

(2) It was found that heavily doped ZnSe:Al layers show two nonradiative trap centers ND1 and ND2 near the conduction-band minimum (CBM). ND1, positioned at 0.2 eV below the CBM, was expected to have little influence on electron trapping due to its low trap density of 2×10^{15} cm^{-3}. However, ND2 is expected to be a dominant electron -trap center due to its large trap density of 3×10^{16} cm^{-3}, positioned at 0.8 eV below the CBM. The emission peak of ND2 shifted to the low temperature side with increasing a filling pulse voltage due to the Poole-Frenkel effect. Moreover, ND2 is ascribed to extended defects, which showed the anomalous behaviors: the emission peak with increasing filling-pulse duration; the broad emission half width; the nonexponential capacitance-transient curve.

(3) It was found that a heavily doped ZnSe:Al layer shows large photocapacitance and has one nonradiative trap center ND3 near the valence-band maximum (VBM), while a lightly doped ZnSe:Al layer shows only weak photocapacitance.

In terms of the extensive studies using PL, DLTS, and PHCAP, we found three nonradiative trap

centers (ND1 and ND2 below the CBM and ND3 above the VBM) and two radiative trap centers (RD1 and RD2 above the VBM) in heavily Al-doped ZnSe layers. Among them, ND1 showed much weak signal intensity, which means its contribution is minor. And, ND2, even if it has a trap density larger than ND1, exhibited that its trap density and activation energy are not affected by Al incorporation. However, it was found that RD1, RD2, and ND3 are generated by Al incorporation and their effect is enhanced by increasing incorporating Al. This means that the electrical and optical degradation of heavily doped ZnSe:Al layers is caused by RD1, RD2, and ND3. Moreover, we should note that the deep levels exist above the VBM. Consequently, it is suggested that the deep levels degrade the luminescence efficiency and electron mobility of ZnSe layers, besides causing the carrier compensation of electron concentration.

Second, we have investigated the deep levels of ZnO layers grown by MBE on GaN templates. ZnO layers naturally have n-type conductivity, which is ascribed to the deep levels induced by unintentionally formed native defects. Purpose of this work is investigate the deep levels that exist in ZnO epitaxial layers, while previous researches concentrated on polycrystalline and single crystalline bulk ZnO. First work for capacitance studies is to fabricate Schottky contacts to ZnO layers. However, the presence of conducting layers on the surface of thin film ZnO makes it difficult to fabricate Shottky contacts to ZnO films for capacitance studies. Moreover, the sample structures used in this work are composed of ZnO/GaN heterostructures. Consequently, it is expected that the C-V characteristic curves reflect ZnO/GaN heterointerface.

(1) In the study of Au/ZnO:N Schottky contacts, it was found that the Schottky characteristics are dependent on the growth temperature and polar direction of ZnO:N layers. Moreover, it was found that the Shottky barrier height is proportional to the resistivity and incorporated N concentration in ZnO:N layers. As a result, a Schottky contact with a barrier height of 0.68 eV and an ideality factor of 1.8 could be otained. Consequently, it is suggested that the low growth temperature and Zn-polar direction are favored for the N incorporation in ZnO:N, which contributes to the increased resistivity in ZnO:N layers and results in good Schottky characteristics.

(2) In the study of ZnO/GaN heterostructures, it was found that C-V characteristic curves have a peculiar form: large plateau regions in C-V curves; rapid increase at the heterointerace in the depth profile of

electron concentration. They are ascribed to the confined charges caused by large conduction-band discontinuity at the ZnO/GaN heterointerface. Especially, a ZnO:N/GaN heterostructure exhibited a large plateau region of 10 V and a high electron concentration of ~ 10^{19} cm^{-3} at the heterointerface. This indicates that the heteointerface of ZnO/GaN is electrically degenerate and a 2-dimensional electron gas is formed. This means that the ZnO/GaN heterostructure is a promising material for HEMTs.

(3) In the study of deep levels in ZnO layers using AS, it was found that ZnO layers are suffered from relatively shallow trap centers. Frequency-dependent capacitance measurements showed that ZnO layers grown under Zn-rich and stoichiometric flux conditions suffer from larger dispersion than a ZnO layer grown under an O-rich flux condition. Temperature-dependent capacitance measurements revealed that all the ZnO layers have shallow trap centers ET1 and deep trap centers ET2, while the Zn-rich ZnO layer had another shallow trap center ET3 besides ET1 and ET2: the thermal activation energies of ET1, ET2, and ET3 are estimated to be 0.033 ~ 0.046 eV, 0.12 ~ 0.15 eV, and 0.065 eV, respectively. Moreover, it was exhibited that the density of ET2 is larger than those of ET1 or ET3 in all cases and increases as the Zn/O flux ratio increases. Consequently, it is suggested that the large dispersion effect observed in the Zn-rich and stoichiometric ZnO layers is ascribed to the high density of deep electron-trap center ET2.

In conclusion, the present thesis studies deep levels in ZnSe and ZnO layers grown by MBE. Based on the present studies, it is expected to find a way to control defects in ZnSe and ZnO layers, which will enable to control both optical and electrical properties of Zn compound semiconductors.

論文審査結果の要旨

代表的なII-VI族ワイドキャプ半導体であるZnSeやZnOは直接遷移のバンド構造を持ち、可視から紫外領域にわたる光素子材料としてとしてポテンシャルが高い半導体材料である。光素子の作製において不純物ドーピングによる伝導制御は最も重要なポイントであるが、一般的に不純物ドーピングは真性欠陥や複合欠陥を形成する。これらの欠陥は、バンドギャプ中に深い準位を形成し、半導体材料の電気的特性及び光学的特性を劣化させる。すなわち、これらの深い準位は多数キャリヤや少数キャリヤをトラップし非発光センターを形成することによって、光素子発光強度の減少、キャリヤ補償による素子動作抵抗を高抵抗化などのデバイス劣化を惹き起こす。従って、光素子研究・開発には深い準位の制御は非常に重要であり、半導体物理だけでなく半導体デバイスにおいて、深い準位の評価は極めて重要な研究課題である。本論文の目的は、亜鉛化合物半導体、特に、ZnSeやZnOエピタキシ膜中の深い準位を明らかにし、深い準位制御のための知見を得て、良好な特性を持つ光素子開発に寄与する事である。

本論文は全6章より構成されている。

第一章は序論であり、光素子半導体材料・デバイスの研究背景を述べるとともに、亜鉛化合物II-VI族半導体の従来の研究状況、研究課題を明らかにするとともに本研究の目的を設定する。

第二章は実験技術に関する。本研究で深い準位の評価に用いたフォトルミンセッセンス法、ホール測定、過渡容量法による深い準位測定（深準位過渡分光法（DLTS法）、フォトキャパシタンス法、アドミッタンススペクトロスコピー等）について測定の原理と実験に用いた装置の詳細について記している。

第三章は本研究で用いたAlドープZnSeエピタキシ膜とZnOエピタキシ膜の分子線エピタキシ成長に関する。

第四章はAlドープZnSeエピタキシ膜中の深い準位評価に関する。Alドープ ZnSeエピタキシ膜は光素子応用に重要であるが、Alドープ ZnSeエピタキシ膜中の深い準位に関する研究結果は報告されていない。高濃度Alドープ ZnSe層ではAl濃度が $10^{19}cm^{-3}$ 以上になるとは電子濃度の飽和が観測されるが、それとともにバンド端発光強度が減少することをまず明らかにした。さらに高濃度Alドープ ZnSe層中の発光センター(RD1 and RD2)と非発光センター(ND1, ND2, and ND3)を見出し、光特性や電気特性の悪化はRD1(E_v + 0.83 eV)、RD2(E_v + 0.55 eV)、ND3(E_v + 0.45 eV)による事を明らかにするとともに、RD1は$Al_{Zn}V_{Zn}$複合欠陥、RD2はV_{Zn}複合欠陥によることを示した。

第五章はZnOエピタキシ膜中の深い準位評価に関する。本研究は過渡容量法によるZnOエピタキシ層の深い準位に関する最初の研究である。ZnO層は高い残留電子濃度によって漏洩電流が大きく、良好なショットキ電極の製作が難しい。ショットキー電極作成技術を開発し、これを基にして過渡容量法によって、三つの電子トラップ準位ET1 (E_c - 40 meV)、ET2 (E_c - 0.14 eV)、ET3 (E_c - 65 meV)を検出することに成功した。ET1 とET2はZnO層に共通的に観察され、ET3は格子間Znによることを示した。

第六章は結論であり、本研究を総括している。

以上要するに、本研究はワイドギャップ光半導体材料であるZnSeやZnOなどの亜鉛化合物半導体エピタキシ膜中の深い準位を明らかにしたものであり、応用物理学、半導体工学、結晶工学に寄与するところ大である。

よって，本論文は博士(工学)の学位論文として合格と認める。